

MECHANISMS FOR TRACE ELEMENT ENRICHMENT IN FLY ASH DURING COAL COMBUSTION

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INTRODUCTION

It is now well established that the smaller flyash particles formed during coal combustion show a significant enrichment of several volatile trace elements. The most widely accepted model for trace element enrichment in flyash formation involves the volatilization of these elements during combustion, followed by condensation or adsorption over the available matrix material (composed primarily of the nonvolatile oxides of Al, Mg, and Si) (1). The larger surface-to-volume ratio of the smaller particles leads to a trace element concentration in the free molecule regime (2) which is inversely related to the particle diameter. Indeed, flyash surfaces have been found to be enriched in several of the same trace elements showing enrichment in the smaller particles, supporting this mechanism (3-5). The smaller particles, which show the highest concentrations of several trace metals, are not efficiently collected by pollution control devices. These particles, enriched in potentially toxic trace metal, also have the highest atmospheric mobilities and are deposited preferentially in the pulmonary and bronchial regions of the respiratory system (1). A proper understanding of the trace element enrichment mechanism is a necessary prerequisite for the prediction of the environmental impact of coal-fired plants, as well as for improving the efficiency of pollution control devices.

Our goal is to determine the mechanism for flyash formation, the enrichment of certain elements in the smaller flyash particles, and the identity of the trace inorganic and organic products of coal combustion. In the initial phase of this study, our investigations have centered on the areas described below.

A. Surface Studies and Flyash Characterization

Studies of fly ash and flyash surfaces have been undertaken using photoelectron spectroscopy, proton induced X-ray emission, secondary ion mass spectrometry, Rutherford backscattering, and scanning electron microscopy. Several of these techniques were used in conjunction with sputtering to obtain concentration vs. sputtering depth profiles. Extensive studies have also examined the various types of flyash particles as a function of particle size and other characteristics. These studies have provided qualitative and semi-quantitative evidence showing the enrichment of several volatile trace elements on flyash surfaces.

B. Flyash Volatilization

On the assumption that species volatilized during combustion and condensed on flyash surfaces may be readily volatilized on heating, two experiments were designed to identify the volatile species. First, flyash samples were activated, and heated to temperatures up to 1400°C and the volatile components collected for neutron activation analysis. Volatilization vs. temperature profiles have been obtained for several elements including Se, Hg, Br, I and As. Second, flyash samples were heated up to 2000°C in a Knudsen cell and the volatile species analyzed by modulated molecular beam mass spectrometry; hence, obtaining information on the actual molecular species volatilized.

C. Extractions of Organic Matter

The organic fraction of the collected fly ash has been extracted from sized flyash fractions by both solvent extractions and a vacuum extraction of fly ash heated slowly to 400°C. These fractions have been analyzed by GC and GC/MS techniques.

D. Analysis of Sized Flyash Fractions

Flyash samples collected from the precipitators of two western coal-fired steam plants were separated into size fraction using a Bahco Microparticle Classifier. Separate aliquots of each size fraction were analyzed for 43 major, minor and trace elements by X-ray fluorescence (XRF), atomic absorption (AA), and instrumental neutron activation (INAA), to establish the concentration-particle size dependence for each element. Replicate analyses of two separate size fractions have allowed us to assess the heterogeneity of the fly ash and sampling errors. Analytical results for the "best method" are collected in Tables 1 and 2; analytical results for the second coal-fired plant for a wider range of particle sizes ($<0.2\mu$ to $>150\mu$) have also been obtained. These results provide information on trace element enrichment in submicron flyash particles.

RESULTS AND DISCUSSION

The analysis of well-defined flyash size fractions offers the most promising method for determining the controlling mechanisms in the volatilization-condensation processes. Surface-depth profiles from sputtering are semi-quantitative (at best), are not usually sensitive to trace elements, and are often dependent on the simultaneous examination of a "field" of particles (or of individual particles, with added problems resulting from low sensitivity and the heterogenous nature of fly ash). These studies also carry the implicit assumption that diffusion will not significantly disturb the surface-depth profile after condensation. The observation of crystal growth on flyash particles(6) makes this assumption dubious. On the other hand, the major requirements for concentration vs. particle size measurements are much more readily fulfilled; the major assumption being that after condensation interparticle diffusion is negligible.

Elemental analyses of fly ash have often shown an inverse concentration dependence upon particle size for many trace elements. This relationship has been rationalized in terms of a Volatilization-Condensation Model (VCM)(1). According to this model, trace elements volatilized during the combustion process condense upon the (mostly) spherical particles of unvolatilized material in the cooler post-combustion region. The larger surface-to-mass ratio of smaller particles results in an enrichment of the volatilized trace elements, having an inverse or an inverse squared dependence upon particle diameter, depending upon the flow regime [i.e., free molecule or continuum](1,2).

The VCM, as proposed by Natusch and coworkers(1,7), predicts an inverse dependence of the total concentration (C) upon particle diameter,

$$C = C_m + \frac{6C_s}{\rho D} \quad 1)$$

where C_m is the concentration in the matrix upon which the volatiles condense, C_s is the surface concentration, ρ is the density, and D is the particle diameter. Flagan and Friedlander, however, have recently suggested that a direct dependence of C on D^{-1} should exist only in the free molecule regime where the Knudsen number, Kn , is greater than 1(2). At lower values of Kn , in the continuum regime, they suggest that the total concentration will be proportional to D^{-2} . This corresponds to a

surface layer thickness which is greater for smaller particles (proportional to D^{-1}) and predicts a much greater increase in the concentration of volatilized elements for the smaller particle sizes.

To compare models we have obtained least squares fits of our experimental results to the models of Natusch and coworkers(1) and Flagan and Friedlander(2). The model of Natusch and coworkers(1), with only a few exceptions, provides a significantly better fit than the Flagan and Friedlander model(2) to the data. In the following discussion we implicitly assume a concentration dependence similar to the VCM of Natusch and coworkers.

In order to increase the flexibility of the VCM it is advantageous to generalize the model by assuming a discrete surface layer of thickness L to be deposited over all particles. The relationship between the bulk concentration (C), the concentration in the matrix (C_m), and the concentration in the surface layer (C_s) of thickness L is:

$$C = \frac{C_m d_m (D - 2L)^3 + C_s d_s D^3 - C_s d_s (D - 2L)^3}{d_m (D - 2L)^3 + d_s D^3 - d_s (D - 2L)^3} \quad (2)$$

where

D = particle diameter

d_m = density of matrix material

d_s = density of surface layer

Results of analyses of fly ash as a function of particle size indicate that the elements, Mn, Ba, V, Cr, Co, Ni, Cu, Ga, Nd, As, Sb, Sn, Br, Zn, Se, Pb, Hg and S, are mostly volatilized in the combustion process (Table 1). The elements, Ti, Al, Mg, Na, K, Mo, Ce, Rb, Cs and Nb, appear to have a smaller fraction volatilized during coal combustion. The remaining elements, Si, Fe, Ca, Sr, La, Sm, Eu, Tb, Dy, Yb, Y, Sc, Zr, Ta, Na, Th, Ag and In, are either not volatilized or show trends which are not readily rationalized in terms of the simple VCM (Table 2).

Figure 1 shows the concentration vs. particle size data plotted for As, Zn, Rb and Mn, which are typical of elements having behavior which may be attributed to volatilization during combustion. These data have been fitted to the VCM using Equation 2, indicated by the lines in Figure 1.

The elements listed in Table 2 show either very little enrichment in the smaller particles or unusual concentration profiles. The concentration of Si shows a definite direct dependence upon particle size, making it unique in this study (Figure 2). The VCM can be used to qualitatively rationalize the Si data; by assuming $L = 0.1\mu$, $C_m = 35.5\%$, and $C_s = 0$ (and $d_m = d_s$), one obtains the fit given by the line in Figure 2.

The most interesting trends with particle size are observed for a group of elements (Ca, Sr, La, Sm, Eu, Tb, Dy, Yb, Y, Sc and Th) which exhibit distinct maxima in concentration at an intermediate particle size (4-8 μ). These trends are most striking for Ca and Sr (Figure 3), where maxima at ~4 μ are observed, confirmed by analysis of different samples by AA, XRF and INAA. The similarity of Ca, Sc, Sr and Y, and the rare earth elements is not surprising; these elements are known to be chemically similar. Barium might also be expected to behave in a similar fashion, but its lower oxide boiling point apparently results in sufficient volatility to obscure these trends. Concentration profiles for several of the rare earth elements

are shown in Figure 5. In Figure 6 we have plotted the rare earth element (REE) abundances normalized to chondritic values: The REE pattern observed for fly ash is similar to that observed in apatite, a mineral containing high concentrations of the rare earth elements and present as an accessory mineral in rocks and soils. (Similar REE patterns are also commonly observed for coal, plant and soil samples.) There are two plausible explanations for the observation of a maximum at $\sim 5\mu$, one involving geochemical fractionation, and the second, a combined geochemical-volatilization mechanism. The first involves an introduction of a geochemical fractionation mechanism to explain a maximum in the concentration vs. particle size profile at $\sim 4\mu$. The second couples a more reasonable geochemical fractionation process with the VCM. By assuming a decreasing value of C_m with particle size, setting $C_s = 0$ and choosing a finite surface layer thickness (L), one can obtain maxima in the concentration profiles; a condensed layer 0.1μ thick can rationalize a maximum at $\sim 5\mu$. Since the concentration profile resulting from any geochemical fractionation mechanism is unknown, a precise estimate of L is impossible. However, values of $L > 0.05\mu$ would be required to explain the results. To determine the relative importance of possible geochemical fractionation mechanisms, samples of the mineral matter obtained by solvent cleaning and low temperature ashing of coal have been sized and subjected to chemical analysis.

Analysis of the results in Table 1 (and Figure 1) shows that many elements are only partially volatilized during combustion, whereas others are essentially completely volatilized. Attempts to rationalize the volatility of elements in terms of simple parameters, such as the boiling points or melting points of the elements, their oxides, or sulfides are only partially successful, the best being the correlation with oxide boiling points. This is reasonable since oxides are known to account for the bulk of the fly ash and the "inorganic" elements in coal often exist as oxides, or form the oxide upon heating. While a rough correlation with oxide boiling points does exist, there are several elements with oxide boiling points above 1600°C which show appreciable enrichment in fly ash, including Cu, B, Tl, Zn, Ba, Ga, Cr, Mn, U and Be. A similar lack of correlation is observed for elements with oxide boiling points of less than 1500°C , with several elements showing only limited volatility (e.g., Cs, Li, Rb and Na).

The reasons for the enhanced volatility of specific elements may be either physical or chemical. The amount of trace element volatilization which will occur during coal combustion will be dependent upon a number of physical parameters, the most important being the residence time in the furnace and the concentrations and temperature vs. time profiles for both the gas and particulate phases.

The "inorganic" elements (defined here as all elements other than C, H, S and N) usually account for between 2% and 40% of the coal by weight, with a range of 5% to 15% being most common. While inclusions of mineral matter account for the bulk of the inorganic elements in coal, specific trace elements may be primarily associated with the organic fraction of coal.

The trace elements associated with the organic fraction of coal will be especially important in determining the gaseous and particulate emissions from coal combustion. During combustion, trace elements which are trapped in an organic matrix, or bonded in organic compounds (organometallic species), may be volatilized, or form an aerosol of minute particles. These elements may have a much higher probability of being transferred to the vapor state than a similar compound associated with the mineral fraction. It should be noted, however, that a volatilization of the organically associated elements is unnecessary for trace element enrichment; a similar inverse dependence of concentration upon particle size will result as the coal is consumed, and nonvolatilized inorganic elements associated with the organic fraction ultimately deposit on the remaining mineral inclusions which

finally form the fly ash. Organically associated elements which are not volatilized (or atomized) will be agglomerated with the mineral inclusions as the coal particles shrink during the pyrolysis and combustion processes. The precise concentration vs. particle size dependence predicted by this model depends on the relationship between the initial coal particle size and the size of the mineral inclusion.

Since insufficient information is available to determine a reasonable model, and the fraction of organically associated elements volatilized [or existing in the gas phase as fine particles, which will heterogeneously condense on larger particles (2)] is unknown, we cannot predict the precise concentration dependence of organically associated elements. However, the concentration of organically associated elements will be inversely dependent upon particle size, and may be qualitatively described by the VCM. Thus, the organically associated elements (which account for more than 50% of several elements) must play an extremely important role in the trace element enrichment observed in emitted flyash particles. To examine this theory we have begun sink-float separations of coal samples to determine the organic affinity of various elements in the feed coal at a coal-fired plant. These results will be compared with flyash enrichment data in our presentation.

The relationship between the percent of ash volatilized during coal combustion and the surface layer thickness in the VCM may be explored if the particle size distribution is known. As an approximation we have used the size distribution data obtained by Schulz et al. (8), and fit their results to a log-normal distribution (Figure 4). Assuming surface layer thicknesses of 0.01μ and 0.1μ (and $d_s = d_m$), one can integrate over the size distribution and determine that 5% and 28%, respectively, of the total ash was volatilized during combustion.

In Figure 4 we have also plotted the cumulative volume of the surface layer (V_s) over the total volume of all particles (V_t), as a function of particle size for a surface layer thickness of 100\AA . This analysis shows that for elements completely volatilized (assuming $d_s = d_m$), half of their total mass will be in particles of 0.33μ or smaller, and that more than 50% will be in particles between 0.1μ and 1.0μ in diameter. This result is especially important since there is a minimum in the collection efficiencies of most emission control devices in the same size regime.

In general, and despite its simplicity and crude approximations, the VCM appears to predict the concentration vs. particle size dependence remarkably well. While the agreement may be fortuitous, as a result of the complex gas-particle and particle-particle interactions during combustion which are only partially understood (2), the VCM does provide a good empirical fit to the data, using parameters which may be rationalized in terms of the chemical nature of coal. Our analysis has shown the organically associated elements, which are a major fraction of many trace elements in coal, play an important role in the enrichment of the smaller size particles and, hence, the emissions from coal-fired plants.

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TABLE 1

Concentrations as a Function of Particle Size for Elements Showing Enrichment in the Smaller Size Fractions^a

Diameter ^b	Element													
	Ti ^c (%)	Al ^d (%)	Mg ^e (%)	Na ^d (%)	K ^d (%)	Mn ^c	Ba ^c (%)	V ^d	Cr ^d	Co ^d	Ni ^d	Cu ^c	Ga ^c	Nd ^d
0.5	0.79	10.7	2.33	2.05	1.41	954	1.23	340	230	25.7	190	501	96	83
2.0	0.78	10.0	2.29	1.85	1.24	701	0.78	300	220	22.4	130	396	77	80
4	0.82	10.6		1.78	1.33	646	0.62	320	220	22.4	105	345	70	83
5	0.75	9.56	2.15	1.79	1.20	505	0.45	240	140	19.0	67	275	52	50
8.5	0.69	9.35	1.94	1.47	1.11	430	0.34	200	150	16.2	80	241	33	55
12.5	0.34	8.80	1.10	1.20	0.89	262	0.21	110	75	10.0	36	156	14	45
15.5	0.59	7.31	1.37	1.08	0.94	248	0.20	105	90	11.7	63	131		50
25	0.54	6.95	0.82	0.76	0.72	190	0.31	74	60	7.6	35	105	5.4	32
50	0.47		0.61			148						67	4.7	

Diameter ^b	Element													
	Mo ^c	Ce ^d	Rb ^d	Cs ^d	As ^c	Sb ^d	Sn ^c	Br ^c	Nb ^c	Zn ^c	Se ^d	Pb ^c	S ^c	
0.5	87	180	62.1	5.01	79	23.5	51	6.2	74	215	68	254	7920	
2.0	74	170	56.1	4.60	70	22.9	38	4.8	44	162	44	172	5060	
4	76	180	54.6	4.48	67	21.6	28	4.0	50	122	30	139	5120	
5	54	145	51.8	3.60	46	13.6	10	3.2	40	87	23	96	4150	
8.5	36	135	46.2	3.36	29	11.0	9	1.6	35	70	12	74	3100	
12.5	16	110	43.1	2.89	10.5	4.20		0.9	33	32	10	44	1440	
15.5	15	100	34.8	2.57	10.1	3.40	8	<0.7	30	30	8	41	<1500	
25	10	80	34.7	2.20	4.6	1.96		<0.6	27	20	5	22	<1500	
50	9				4.2			<0.6	16	10		17	<1500	

a. Concentrations given in PPM unless otherwise noted.

b. Mass median diameter.

c. By XRF.

d. By INNA.

e. By AA.

TABLE 2

Concentrations as a Function of Particle Size for Elements
Not Showing Enrichment in the Smaller Size Fractions^a

Diameter ^b	Element							
	Si ^c (%)	Fe ^e (%)	Ca ^d (%)	Sr ^e	La ^e	Sm ^e	Eu ^e	Tb ^e
0.5	21.9	3.47	5.14	1600	70.3	8.68	1.95	1.15
2	23.5	3.20	6.16	2080	73.7	10.9	2.14	1.5
4		3.22	6.71	2360	76.7	10.5	2.29	1.6
5	24.3	2.89	6.53	1720	72.8	10.1	2.17	1.4
8.5	26.7	2.66	5.99	1650	69.6	9.43	1.97	1.3
12.5	29.4	2.10	3.33	1270	53.4	5.92	1.49	1.1
15.5	29.4	2.20	3.16	1520	55.7	7.23	1.56	1.2
25	34.3	3.02	2.26	800	41.9	6.00	1.16	0.86
50	35.8		2.01	(600) ^d				

Diameter ^b	Dy ^e	Yb ^e	Y ^d	Sc ^e	Zr ^d	Ta ^e	Th ^e
0.5	7.3	4.26	48	24.6	280	3.2	32.6
2	8.7	4.69	54	26.8	290	3.0	35.2
4	9.6	4.79	61	28.7	306	2.9	37.6
5	8.8	4.96	55	26.9	330	2.7	58.2
8.5	7.8	5.00	49	24.7	320	2.8	32.8
12.5	6.6	3.47	37	17.7	350	2.1	25.6
15.5	7.1	3.49	36	18.5	440	2.1	28.4
25	4.7	3.33	32	13.7	624	1.8	22.8
50			28		374		

a. Concentrations in PPM unless otherwise noted.

b. Mass median diameter (microns).

c. By AA.

d. By XRF.

e. By INAA.

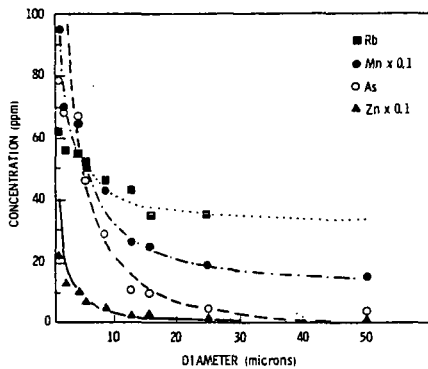


FIGURE 1. CONCENTRATION VERSUS PARTICLE SIZE DATA FOR Mn, Rb, As and Zn. ALSO GIVEN IS THE BEST FIT TO THE VOLATILIZATION-CONDENSATION MODEL

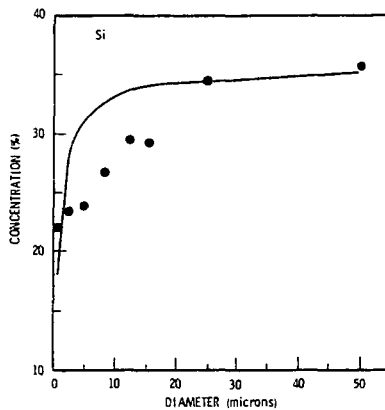


FIGURE 2. CONCENTRATION VERSUS PARTICLE SIZE DATA FOR SI WITH BEST FIT TO THE VCM ASSUMING A 0.1μ SURFACE LAYER THICKNESS

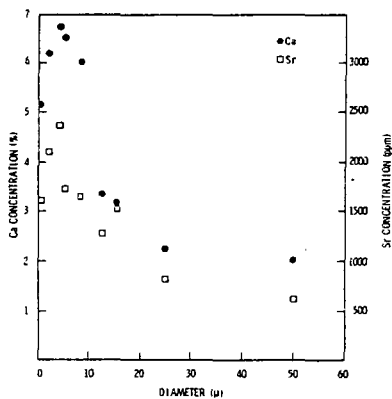


FIGURE 3. CONCENTRATION VERSUS PARTICLE SIZE DATA FOR Ca (●) AND Sr (□). A MAXIMUM WAS OBSERVED FOR BOTH ELEMENTS, AND MOST OF THE RARE EARTH ELEMENTS (TABLE 2), AT APPROXIMATELY 5μ . THE DATA FOR Ca AND Sr WERE CONFIRMED BY COMPARISONS OF ANALYSES BY AA, XRF, AND INAA TECHNIQUES

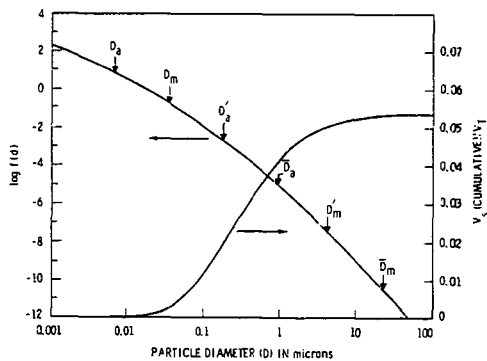


FIGURE 4. LOG-NORMAL DISTRIBUTION OF PARTICLE SIZES ASSUMED TO RESULT FROM COAL COMBUSTION (LEFT). D_a IS THE DIAMETER OF AVERAGE AREA, D_m IS THE DIAMETER OF AVERAGE MASS, D'_a IS THE AREA MEDIAN DIAMETER, D'_m IS THE AREA MEAN DIAMETER, D'_m IS THE MASS MEDIAN DIAMETER, AND D_m IS THE MASS MEAN DIAMETER. ALSO GIVEN IS THE CUMULATIVE FRACTION OF THE TOTAL VOLUME OF THE FLYASH PARTICLES DUE TO A SURFACE LAYER 0.01μ THICK (RIGHT) FOR THIS LOG-NORMAL DISTRIBUTION

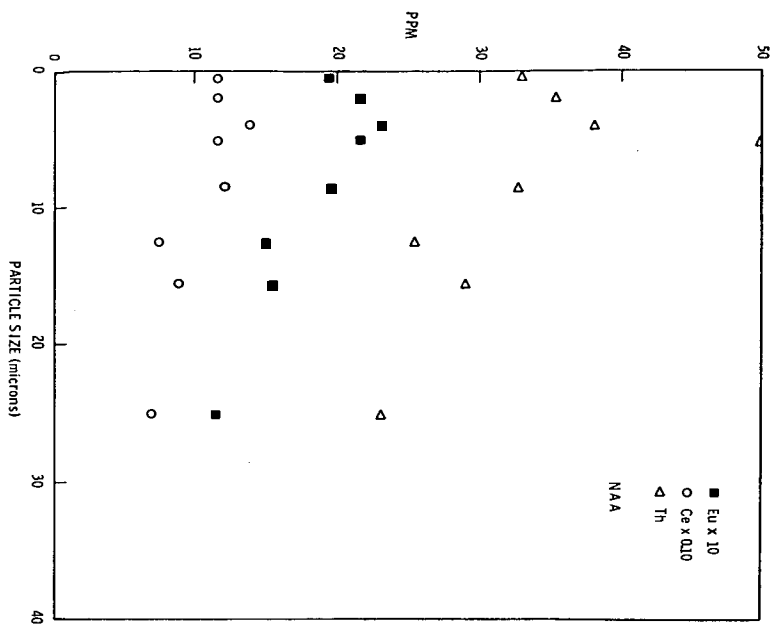


FIG. 5 (left) CONCENTRATION OF RARE EARTH ELEMENTS (REE) FROM NAA
AS A FUNCTION OF PARTICLE SIZE
FIG. 6 (above) RARE EARTH ELEMENT (REE) ABUNDANCES NORMALIZED TO
CHONDRITES FOR TWO PARTICLE SIZES

